

12/04/98  
JC595 U.S. PTO

JC511 U.S. PTO  
09/205297  
12/04/98

12/04/98

# BIRCH, STEWART, KOLASCH & BIRCH, LLP

INTELLECTUAL PROPERTY LAW

8110 GATEHOUSE ROAD  
SUITE 500 EAST  
FALLS CHURCH, VA 22042

U S A

—  
(703) 205-8000

—  
FAX: (703) 205-8050  
(703) 698-8590 (G IV)

e-mail mailroom@bskb.com  
web: http://www.bskb.com

SENIOR COUNSEL:  
ANTHONY L. BIRCH  
GARY D. YACURA  
THOMAS S. AUCHTERLONIE  
MICHAEL R. CAMMARATA  
JAMES T. ELLER, JR.  
SCOTT L. LOWE  
JOSEPH H. KIM, PH.D.\*  
RICHARD S. MYERS, JR.\*  
MARY ANN CAPRIA  
MICHAEL J. CORNELISON\*  
MARK J. NUELL, PH.D.  
ROBERT V. RACUNAS  
DARIN E. BARTHOLOMEW\*

REG. PATENT AGENTS:  
FREDERICK R. HANDREN  
ANDREW J. TELEZ, JR.  
MARYANNE LIOTTA, PH.D.  
MAKI HATSUMI  
D. RICHARD ANDERSON  
STEVEN P. WIGMORE  
ESTHER H. CHIN  
MIKE S. RYU  
W. KARL RENNER  
CRAIG A. McROBBIE  
PAUL C. LEWIS

TERRELL C. BIRCH  
RAYMOND C. STEWART  
JOSEPH A. KOLASCH  
JAMES M. SLATTERY  
BERNARD L. SWEENEY\*  
MICHAEL K. MUTTER  
CHARLES GORENSTEIN  
GERALD M. MURPHY, JR.  
LEONARD R. SVENSSON  
TERRY L. CLARK  
ANDREW D. MEIKLE  
MARC S. WEINER  
JOE MCKINNEY MUNCY  
ROBERT J. KENNEY  
C. JOSEPH FARACI  
DONALD J. DALEY  
JOHN W. BAILEY  
JOHN A. CASTELLANO, III

OF COUNSEL:  
HERBERT M. BIRCH (1905-1996)  
ELLIOT A. GOLDBERG\*  
WILLIAM L. GATES\*  
EDWARD H. VALANCE  
RUPERT J. BRADY (RET.)\*

\*ADMITTED TO A BAR OTHER THAN VA.

Date: December 4, 1998  
Docket No.: 2577-106P

Assistant Commissioner for Patents  
BOX PATENT APPLICATION  
Washington, D.C. 20231

Sir:

Transmitted herewith for filing under 37 C.F.R. §1.51, is a Continuation-In-Part application of PCT application no. PCT/GR97/00018 filed on June 5, 1997. The present application is filed on behalf of the inventor(s) according to the provisions of 37 C.F.R. §1.41(c).

Inventor(s): VALKANAS, George N.; KONSTANTAKOPOULOS, Ioannis

For: METHOD AND PRODUCTS TO ABSORB OIL AND ORGANIC SOLVENTS FROM WATER AND FROM SEA

Enclosed are:

A specification consisting of 12 pages  
        sheet(s) of        drawings  
 An assignment of the invention  
 Certified copy of Priority Document(s)  
 Executed Declaration in accordance with 37 C.F.R. § 1.64 will follow  
 Information Disclosure Statement, PTO-1449 with reference(s)

— A verified statement (       Original       Photocopy) to establish small entity status under 37 C.F.R. § 1.9 and 37 C.F.R. § 1.27

Preliminary Amendment

Information Sheet

Priority of International Application No. PCT/GR97/00018 filed on June 5, 1997 is claimed under 35 U.S.C. §120.

— Amend the specification by inserting before the first line thereof the following:

--This application is a Continuation-In-Part of PCT application no. PCT/GR97/00018 filed on June 5, 1997, which designated the United States and on which priority is claimed under 35 U.S.C. §120, the entire contents of which are hereby incorporated by reference.--

Priority of Application No. 960100185 filed in Greece on June 5, 1996 is claimed under U.S.C. §119.

— Other \_\_\_\_\_

The filing fee has been calculated as shown below:

		LARGE ENTITY		SMALL ENTITY	
BASIC FEE		\$760.00		\$380.00	
	NUMBER FILED	NUMBER EXTRA	RATE	FEE	RATE
<b>TOTAL CLAIMS</b>	6 - 20 =	0	x 18 = \$		x 9 = \$
<b>INDEPENDENT CLAIMS</b>	1 - 3 =	0	x 78 = \$		x 39 = \$
<b>MULTIPLE DEPENDENT CLAIMS PRESENTED</b>			+ \$260.00		+ \$130.00
<b>TOTAL</b>			<b>\$1020.00</b>		

A check in the amount of \$ 1020.00 to cover the filing fee and recording fee (if applicable) is enclosed.

— Please charge Deposit Account No. 02-2448 in the amount of \$       . A triplicate copy of this transmittal form is enclosed.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By C. Joseph Faraci  
C. JOSEPH FARACI  
Reg. No. 32,350  
P.O. Box 747  
Falls Church, VA 22040-0747  
(703) 205-8000

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicants: VALKANAS, et al

Serial No.: New Group:

Filed: December 4, 1998 Examiner:

For: METHOD AND PRODUCTS TO ABSORB OIL AND ORGANIC SOLVENTS  
FROM WATER AND FROM SEA

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Box Patent Application  
Washington, D.C. 20231

December 4, 1998

Sir:

The following preliminary amendments and remarks are respectfully  
submitted in connection with the above-identified application.

**IN THE CLAIMS:**

**CLAIM 5:** Line 1, change "claims 3 and 4" to --claim 3--

**\*\*\* R E M A R K S \*\*\***

The amendment to the claims merely deletes the undesired multiple  
dependencies and places the application in better form prior to  
examination.

PATENT  
2577-106P

Favorable action on the above-identified application is respectfully requested.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. §1.16 or under 37 C.F.R. §1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By



C. JOSEPH FARACI  
Reg. No. 32,350  
P.O. Box 747  
Falls Church, VA 22040-0747  
(703) 205-8000

CJF/dlg

C

## METHOD AND PRODUCTS TO ABSORB OIL AND ORGANIC SOLVENTS FROM WATER AND FROM SEA

5 The release of organic solvents and of oil into the environment and in water basins leads to disasters. And the consequences of these accidents are the destruction of the environment and the disruption of the chains of life.

10 A most critical such environmental problem is created by the release of oil during the sea transportation because of sea accidents. Another such critical problem directly connected with life is the pollution in sea ports and in enclosed seas around main cities.

15 Such pollution loads are also formed in navigable rivers and in lakes by rejection of petroleum and oil, and also during pumping of petroleum in rivers, in lakes and in sea from the existing there production wells where heavy

20 pollution problems are created.

25 The facing of those environmental problems is up to date unsuccessful, insufficient or incorrect, detergents are used with which the suspended petroleum and oils are emulsified to become bottom sludge deposits. To the sea basin are thus summed huge pollution loads in between and in Mediterranean sea with intense petroleum transportation transportation traffic the pollution loading has become 0.3-0.8 g/liter and the bottom sludge

30 formed exceeds the 2.000 tons/ km<sup>3</sup> which makes a World maximum.

We have dealt in long lasting R & D work with that problem and have developed a solution by which those water and sea pollution accidents are successfully faced

5 because our solution works with absorption of the petroleum and of oils from sea and water surfaces and thus leads to their useful recycling.

We have discovered, constructed and proved in practice

10 polymers multiprocessed to become macroplegmatic and we have proved that these operate with effective absorption of petroleum , of oil and of organic solvents in quantity 30 to 60 times their weight intermolecularly. With external sorption adherence more quantities are absorbed

15 so that totally are collected high quantities of released petroleum and oils into the water basins. The operation of the action is organised with loading those absorption products into a net which is suspended in the water surface and operates like a broom absorbing

20 quantitatively and sweeping all the oily pollution loads which are transported in tanks where those are washed with petroleum and are collected as useful fuel.

As absorbing products are used polymeric products

25 resulted from Polystyrene and copolymers new or recycled in a wide range of composition so that can cover a wide variety of uses. These polymers are processed to become macroplegmatic on structure designed to absorb organic solvents and oil molecularly in pure form or in mixtures

30 according to existing conditions.

The polymers bases in use are the following:

Polystyrene which after special processing becomes macroplegmatic with Mc 50.000.

5

The trimeric copolymer SEBS (Styrene, Ethylene, Butadiene, Styrene) which is specially crosslinked to become macroplegmatic.

- 10 The elastomeric SBR fully hydrogenated with Styrene composition 10%, 20% and 40% which after special cross-linking and processing gave macroplegmatic products of variation in absorbing capacities.
- 15 The cross-linking is advanced in solutions containing those polymers 20-25% in chlorinated hydrocarbon solvents by weight such as dichloroethane with cross-linking agent the 1,4-dichloromethyl-2,5-dimethylobenzene- (DCMDMB) and for catalytic action is used tetrachlorotitanate (TiCl<sub>4</sub>)
- 20 in 10% solution in dichloroethane.

- 25 The appearance of thickness that is the cross-linking result is related to the catalytic action which is added, however, in small quantities in drops and is effective in high solution volumes.

- 30 In the following Tables are given the results of the cross-linking agent to the polymer SEBS in weight ratio in reaction at 60°C. To determine the absorption capacity the porosity is studied which was found to be low up to 4% of cross-linking agent and then to increase.

TABLE

DMDMB ,% SEBS, resulted porosity

5		(cm <sup>3</sup> /g )
	1	0.294
	2	0.204
	4	0.279
	16	0.319
10	32	0.477

It was then studied the absorption capacity of organic solvents selected from market products, derived from petroleum

15 Absorption of Toluene in water- PS

C initial PPM	C final PPM
---------------	-------------

20	413,9	0.68
	102,1	0.59
	363,3	0.78

Absorption of Toluene Water-SEBS

25	410,4	0.4
	319,6	0.39
	119,9	0.37

30

Absorption of 1,2-Dichloroethane -

Water , SEBS

	692,2	0.4
5	202,7	0.56

Absorption of Decane-water, SEBS

	456,2	0.35
10	623,4	0.37

Absorption of Petrol-water ,SEBS

	653,4	0.36
15	638,2	0.34

Absorption capacity of the different absorption products per gram.

20	1	2	3	4
PS	-	-	-	-
SEBS	4,5	7,5	9.0	5,0
SBR (10)	50,0	45.0	40.0	30.0
SBR (20)	48.0	40.0	38.0	25.0
25	5	6	7	8
PS	-	-	-	12
SEBS	8	9.0	6.0	17
SBR(10)	32.0	29.0	33.0	36
30	SBR(20)	27.0	26.0	31.0

	9	10	11	12	13
PS	17	28	25	18	18
SEBS	18	18	12	22	22
SBR (10)	37	-	-	16	15
5 SBR (20)	32	-	-	12	13

1 n-pentane, 2 n-hexane, 3 n-octane, 4 iso-octane, 5 n-nonane, 6 n-decane 7 n-dodecane, 8 benzene, 9 toluene, 10 chloroform, 11 carbon tetrachloride, 12 1,2 dichloroethane, 13 1,1,3 trichloroethane .

With the above results which are successful and very useful we have studied the absorption capacity on oil surface pollution in harbours and the absorption capacity in sea. For these trials the absorption polymers were placed in a polypropylene net in composition 20% PS, 30% SEBS, 30% SBR (10) and 20% SBR (20) and the results obtained were very impressive. And it was proved that the sweeping was not due to endomolecular absorption but also due to external absorption adherence so that the collection of oily matter was very satisfactory. That load of oil matter is brought in a tank and is washed with petroleum by which all those oils are collected as useful fuels. That is this seeping action makes the pollution loads useful and the harbours and the sea as well as the sea bottom are liberated from oily and dirty matter and the ecology is overall improved.

EXAMPLE 1

In a reactor of 0.5 m<sup>3</sup> capacity is brought (a) dichloroethane 200 liter and is added (b) the polymer 5 SEBS 20 kg. and in the solution is added (c) 1,4-dichromethyl -2,5-dichlorobenzene 100 grms and at 60°C is added (d) the catalyst TiCl<sub>4</sub> as 10% solution. After agitation for 40 minutes the cross-linking started and the solution becomes viscous and thick and cannot be 10 agitated further. Then is taken off and is cut in a mincing machine and then is brought to a reactor for taking the solvent out to become commercial product. That reactor is heated up to 170°C under vacuum and stirring so that all the solvent is taken off and the polymeric 15 product is completely deodorised.

Under the same conditions is treated the Polystyrene and the SBR 10%, 20% and 40% in Styrene fully hydrogenated to saturation with the addition of the crosslinking agent in 20 2% in all, calculated on the benzene rings present.

EXAMPLE 2

Products of example 1 in composition quantities 25 Polystyrene 30% , cross-linked SEBS 30% , cross-linked SBR 10% in Styrene ,fully hydrogenated to saturation 20% and SBR 20% in Styrene fully hydrogenated to saturation 20% , are brought on a polypropylene net and are swept along on harbour surface. By sweeping the surface all 30 oily matter is collected in quantity 20% endomolecularly and in quantity 80% adhered externally. The net with the

polymers loaded is brought to a tank and washed with petroleum and the oily matter is recycled as fuel and the absorption polymers are ready to be reutilised.

5

EXAMPLE 3

Products of example 1 in composition quantities 10% crosslinked Polystyrene , 30% crosslinked SEBS , 40% crosslinked SBR ,10% in Styrene fully hydrogenated to 10 saturation, are brought to sweep a sea surface pollution. The oil surface swept was that apart of the main oxidised petroleum mass which is collected otherwise. The materials of the net swept successfully the sea surface being drawn by a boat. All the oily water was collected 15 and the sea net was brought to a tank washing the net with petroleum to receive the absorbed oily matter which was recycled as fuel and the sea and the sea bottom pollution is avoided.

20

EXAMPLE 4

In a lake where is released petroleum and organic solvents from transportation and from production wells, was brought the net of example 3 and is swept on the 25 surface being drawn by a boat. The oily matter swept was by 25% endomolecularly absorbed and by 75% externally absorbed-adhered. It was brought in a tank and washed with petroleum to collect the oily matter absorbed as fuel and the net with the absorbing polymers was recycled 30 to use.

EXAMPLE 5

The polymer net of example 4 is placed at the flow of a  
5 river, the water of which contains oily matter. The  
action on the river was to collect all suspended oily  
matter and the water flow is established with natural  
pure water flow.

CLAIMS

1. Method for producing macroplegmatic polymeric products after special crosslinking treatment wherein  
5 these acquire high potential to absorb organic solvents and petroleum products molecularly enclosed and externally adhered.

10 2. Method according to claim 1 wherein the polymers to be crosslinked to macroplegmatic structures are polystyrene, trimeric copolymer styrene, ethylene and butadiene SEBS (styrene, ethylene, butadiene, styrene) and the elastomeric SBR with 10%, 20% and 40% styrene completely hydrogenated to saturation.

15 3. Method according to claims 1 and 2 wherein those polymers are processed to crosslinking treatment in solutions with chlorinated solvents to acquire macroplegmatic structure of about Mc 50.000 crosslinked with the 1,4-dichloromethyl-2,5 dimethylbenzene (DCMDMB) and with catalyst Titanium Tetrachloride (TiCl<sub>4</sub>) as 10% solution in the chlorinated solvent.

25 5. Method according to claims 3 and 4 by which the polymeric absorbing products are brought in a polymer net in selected mixtures acquiring high ability for sweeping from the water or sea surfaces oily matters by absorbing those endomolecularly and by external adherence.

30

6. Method according to claim 5 by which the absorbed oily mass is brought to a tank and washed with petroleum to collect the absorbed matter as oil and to unload the device net for repeated use.

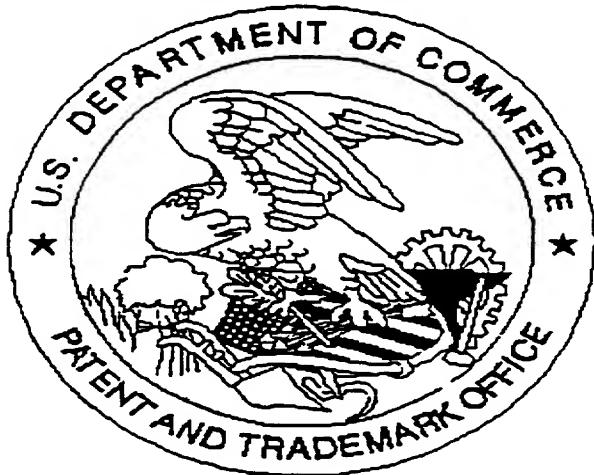
## ABSTRACT

An original method to produce polymeric products is described, which after a special cross-linking become 5 macroplegmatic and acquire ability to absorb organic solvents, petrol and petroleum and products which are released in the water basins or on the sea , 40-80 gram of oily matter/gram of polymers.

The polymers to process are Polystyrene, trimeric 10 copolymer with Styrene, Ethylene, Butadiene (SEBS) elastomeric SBR with Styrene 10%, 20% and 40% fully hydrogenated to saturation, which after special crosslinking in chlorinated solvents with crosslinking agent the 1,4 dichloromethyl -2,5 -dichloro benzene 15 (DCDMDB) and with catalyst the Titanium Tetrachloride (Ti Cl<sub>4</sub>) where at 60°C is formed a thick cross-linked mass which is cut in a mincing machine and the solvent is removed and the polymeric products are deodorised after heating at 170°C with stirring under vacuum.

20 Those products are brought in a polypropylene net and are swept on the surface of water basins, on the surface of harbours and on the surface of sea collecting the oily matter and the petroleum by absorption endomolecularly and by external surface adherence and the loaded net is 25 washed with petroleum to receive all absorbed oily matter as useful fuel and the net with the absorbing polymers is ready for new absorbing action for depolluting with recycling oily matter from water and sea basins.

United States Patent & Trademark Office  
Office of Initial Patent Examination – Scanning Division



Application deficiencies were found during scanning:

Page(s) \_\_\_\_\_ of \_\_\_\_\_ No DECLARATIONS were not present  
for scanning. (Document title)

Page(s) \_\_\_\_\_ of \_\_\_\_\_ were not present  
for scanning. (Document title)

Scanned copy is best available.